

Formation constants of binary & ternary chelates of Ln(III) with maltol & kojic acid in presence of aminocarboxylic acids

M Narasimha Rao, K L Omprakash, A V Chandra Pal* & M L N Reddy

Department of Chemistry, Osmania University,
Hyderabad 500 007

Received 7 March 1988; revised and accepted 6 June 1988

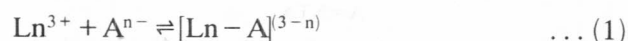
The formation constants of binary and ternary systems involving 3-hydroxy-2-methyl-4-pyrone (HMP) (maltol) and 5-hydroxy-2-hydroxymethyl-4-pyrone (HOMP) (kojic acid), with lanthanide metal ions [La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III)] in the presence of iminodiacetic acid (IMDA), hydroxyethyliminodiacetic acid (HIMDA) and nitrilotriacetic acid (NTA) have been determined in aqueous medium at 30°C and $\mu = 0.1$ M (NaClO₄). The order of stabilities of ternary systems is: HMP > HOMP and IMDA > HIMDA > NTA. These are explained in the light of the basicities of the ligands and charge neutralisation.

In continuation of our earlier studies¹ we report herein the formation constants of binary and ternary systems involving 3-hydroxy-2-methyl-4-pyrone (HMP, maltol) and 5-hydroxy-2-hydroxymethyl-4-pyrone (HOMP, kojic acid), with lanthanide metal ions [La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III)] in the presence of iminodiacetic acid (IMDA), nitrilotriacetic acid (NTA) and hydroxyethyliminodiacetic acid (HIMDA).

Maltol and kojic acid (Fluka), NaClO₄ (E. Merck), NTA and IMDA (Sigma) and HIMDA (Fluka) of AR grade were used as received. The proton-ligand formation constants of the ligands and the metal-ligand formation constants were determined pH-metrically using the Irving-Rossotti titration technique². The formation constants of ternary systems have been evaluated by the method of Ramamoorthy and Santappa³ in aqueous medium at 30°C and 0.1 M NaClO₄.

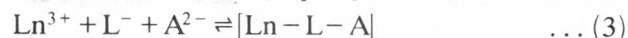
In binary systems the \bar{n} values (0.1 to 1.9) indicate the formation of both 1:1 and 1:2 Ln(III)-L complexes (where L = HMP/HOMP). The metal-ligand formation constants evaluated by various computational techniques like half-integral, linear plots, pointwise calculations and method of least squares^{4,5} are presented in Table 1. The stability order: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) > Y(III) is almost in accordance with the increasing charge/radius ratio of the metal ions⁶.

The ternary complex formation is inferred from the non-superimposability of theoretical composite curve on the experimental curve in the region of mixed-ligand complex formation⁵. The ternary formation curve of Ln(III)-L-A coincides with Ln(III)-A curve (where A = HIMDA or NTA and L = HMP or HOMP) in the lower pH region and its divergence at higher pH region indicates the stepwise formation of the ternary complex. The ligand 'A' acts as primary ligand and the ligand 'L' as secondary ligand [equilibria (1) and (2)]



(where A = HIMDA or NTA and $n = 2$ for HIMDA and 3 for NTA).

In the case of ternary systems involving IMDA the ternary curve deviates from the beginning indicating the formation of the ternary complex in a simultaneous fashion [Eq. (3)]



The ternary formation constants are listed in Table 1. The ternary complexes [Ln-A-L] (where A = HIMDA/NTA and L = HMP/HOMP) formed in stepwise manner are less stable while those formed simultaneously [Ln-IMDA-HMP/HOMP] are more stable as compared to the binary complexes as revealed by $\Delta \log K$ values⁷ (Table 1). The relative order of stabilities [La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) > Y(III)] is the same as that found for binary systems.

The stability order of ternary systems of HMP and HOMP follows the order of the basicities of these ligands, e.g. HMP > HOMP. The order of stability with respect to primary ligands is IMDA > HIMDA > NTA. This could be due to charge neutralisation in forming ternary complexes⁷. In the case of IMDA, coordination occurs with Ln^{3+} to form a neutral metal complex [Eq. (3)]; with HIMDA the coordination of $[\text{HMP}]^- / [\text{HOMP}]^-$ occurs with monopositive $[\text{Ln}-\text{HIMDA}]^+$ primary complex to form neutral complex whereas in the case of NTA, coordination between $[\text{HMP}]^- / [\text{HOMP}]^-$ and neutral primary complex $[\text{Ln}-\text{NTA}]$ occurs to form a negatively charged complex [Eq. (2)]. Therefore greater electrostatic attraction may be expected (i) between Ln^{3+} , $[\text{HMP}]^- / [\text{HOMP}]^-$ and $[\text{IMDA}]^{2-}$; and (ii) between $[\text{Ln}-\text{HIMDA}]^+$ and L^- than between L^- and $[\text{Ln}-\text{NTA}]$ complex.

Table 1—Binary and ternary formation constants* of maltol (L) and kojic acid (L') with aminocarboxylic acids [A¹ = IMDA; A² = HIMDA; A³ = NTA] in aqueous medium[I = 0.1 M NaClO₄; temp = 30°C]

log K	La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)	Y(III)
log K ^M _{ML}	5.22	5.59	5.79	6.01	6.42	5.96
log K ^{ML} _{ML₂}	4.09	4.47	4.82	5.20	5.45	5.14
log K ^M _{MA¹L}	11.74	12.26	12.5	13.43	13.91	13.37
log K ^{MA¹} _{MA¹L}	(5.86)	(5.82)	(6.0)	(6.55)	(7.03)	(6.43)
Δlog K	0.64	0.23	0.21	0.74	0.61	0.67
log K ^{MA²} _{MA²L}	4.95	5.24	5.26	5.73	5.91	5.62
Δlog K	-0.27	-0.35	-0.53	-0.28	-0.51	-0.34
log K ^{MA³} _{MA³L}	4.08	4.36	4.69	5.15	5.30	4.85
Δlog K	-1.14	-0.96	-0.91	-0.61	-0.71	-0.78
log K ^M _{ML'}	5.03	5.15	5.23	5.38	5.72	5.32
log K ^{ML'_{ML'₂}}	3.98	4.5	4.61	4.96	5.13	5.01
log K ^M _{MA¹L'}	11.5	11.91	12.06	12.70	12.96	12.51
log K ^{MA¹} _{MA¹L'}	(5.61)	(5.47)	(5.56)	(5.74)	(6.23)	(5.83)
Δlog K	0.59	0.32	0.33	0.36	0.51	0.54
log K ^{MA²} _{MA²L'}	4.26	4.56	4.77	5.28	5.75	5.21
Δlog K	-0.77	-0.59	-0.46	-0.10	-0.07	-0.09
log K ^{MA³} _{MA³L'}	3.8	4.19	4.32	4.77	5.01	4.54
Δlog K	-1.14	-0.96	-0.91	-0.61	-0.71	-0.78

The values presented in parentheses are the stepwise formation constants evaluated from the simultaneous constants using Sigel's method⁷.

*The deviations are within ± 0.03 log K units.

The distribution of metal among the various metal-ligand species was calculated using the computer program BEST⁸. The maximum percentage of mixed ligand complexes formed are 97%, 80% and 68% for La-HMP-IMDA, La-HMP-HIMDA and La-HMP-NTA species respectively and this is in accordance with the stabilities of mixed ligand complexes.

The authors are grateful to the CSIR, New Delhi for the award of a senior research fellowship to MNR.

References

- 1 Narasimha Rao M, Omprakash K L, Jagannadha Charyulu K, Chandra Pal A V & Reddy M L N, *Acta ciencia Indica*, 12 (1986) 31.
- 2 Irving H & Rossotti H S, *J chem Soc*, (a) (1953) 3397; (b) (1954) 2904.
- 3 Ramamoorthy S & Santappa M, (a) *J inorg nucl Chem*, (1970) 1623; (b) *Indian J Chem*, 9 (1971) 38.
- 4 Omprakash K L, Chandra Pal A V & Reddy M L N, *Indian J Chem*, (a) 21A (1982) 322; (b) 22A (1983) 546.
- 5 Carey G H & Martell A E, *J Am chem Soc*, 89 (1976) 2859.
- 6 Ingle D B & Khanolkar D D, *J Indian chem Soc*, 50 (1973) 190.
- 7 Sigel H, *Angew chem int Edn*, 14 (1975) 394.
- 8 Moitekaitis R J & Martell A E, *Can J Chem*, 60 (1982) 2403.